

BEST AVAILABLE COPY

PCT/EP200 4 / 0 0 7 8 4 1
13 JUL 2004



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

Bescheinigung

Certificate

Attestation

REC'D 22 SEP 2004

WIPO

PCT

Die angehefteten Unterla-
gen stimmen mit der
ursprünglich eingereichten
Fassung der auf dem näch-
sten Blatt bezeichneten
europäischen Patentanmel-
dung überein.

The attached documents
are exact copies of the
European patent application
described on the following
page, as originally filed.

Les documents fixés à
cette attestation sont
conformes à la version
initialement déposée de
la demande de brevet
européen spécifiée à la
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03077382.4

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:
Application no.: 03077382.4
Demande no:

Anmeldetag:
Date of filing: 30.07.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Akzo Nobel N.V.
Velperweg 76
6824 BM Arnhem
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Container with an aqueous solution of a sodium salt of hedta

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B65D/

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

ACD 3014 PDEP

CONTAINER WITH AN AQUEOUS SOLUTION OF A SODIUM SALT OF
HEDTA

The invention relates to a container comprising an aqueous solution of a sodium salt of the chelating compound HEDTA [N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid], and to the use of this aqueous solution for making an iron-chelate complex. The invention further
5 relates to a method for preparing such aqueous solution of said sodium salt of HEDTA.

Some sodium salts of the chelating compound HEDTA are known in the art. For instance, in US 5491259 a method is disclosed for making HEDTA from
10 the trisodium salt thereof. This method makes use of an acidic medium at pH 1.0 to 3.0, resulting to an aqueous feed solution containing protonated HEDTA along with an inorganic sodium salt. This aqueous solution is passed through a diafiltration membrane to separate the organic and inorganic components.

15 Disodium salt of HEDTA is also known. For instance, in EP 54277 and EP 58430 microscopic capsules containing dyestuff suspensions with disodium salt of HEDTA were disclosed.

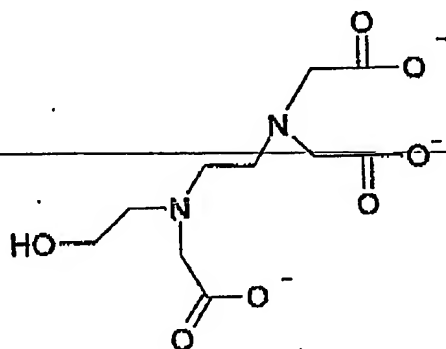
The infrared spectra of HEDTA, and the mono-, di-, and tri-sodium salts of HEDTA have been published in J. Am. Chem. Soc., 85, 311-312 (1963).
20 Commonly, when using HEDTA for chelating ions the trisodium salt of HEDTA is used. Thus according to US 5110965 iron chelates can be made from commercially available 41.3 % aqueous solution of trisodium HEDTA salt by reacting an oxide of iron (as its magnetite) with Na₃-HEDTA and neutralizing the medium to a low pH value with an acid, to obtain the free
25 HEDTA acid.

ACD 3014 PDEP

2

However, the use of the trisodium salt of HEDTA has some major drawbacks when used on a commercial scale. An important problem is the high viscosity of the trisodium salt of HEDTA, which makes the trisodium salt difficult to handle. The high viscosity also limits the practical concentration to values below 45 %. Further, the trisodium salt of HEDTA precipitates at low temperature, making it necessary to heat the containers under such conditions before they can be poured out. It was further found that aqueous $\text{Na}_3\text{-HEDTA}$ solutions are corrosive to aluminum and therefore limits its application to corrosive-proof installations. These problems become particularly relevant when using HEDTA salt in large-scale productions, thus especially when containers with a content of 0,5 kg or more are used. In practice containers can contain 25 to 1000 kg of aqueous HEDTA salt, or even more. It is an objective of the present invention to provide an alternative that has lower viscosity, does not precipitate at low temperature, can be handled in containers at higher concentrations, and has less corrosive properties.

The instant invention provides in containers with salts of HEDTA satisfying the above conditions. To this end it was found that above problems do not occur in containers comprising at least 0.5 kg of an aqueous solution of a sodium salt $x\text{Na}^+y\text{H}^+$ of the chelating compound of formula I:



wherein $x = 2.1 - 2.7$, $y = 0.9 - 0.3$, and $x + y = 3$.

ACD 3014 PDEP

3

The containers of the invention contain at least 0.5 kg of the above solution, preferably at least 1 kg, and most preferably 25 kg or more.

In order to use as less as possible acid for neutralization it is preferred to make an aqueous solution that is as close as possible to the trisodium salt, without having the disadvantages of the trisodium salt. It was found that an optimum regarding the use of neutralization acid, viscosity, precipitation and corrosive properties was obtained for x is about 2.4, for instance within the range 2.3 to 2.5.

It was further found that the salt of the invention could be dissolved in water to a concentration of 45 % or higher without impairing the hereinbefore-mentioned advantages. To satisfy the above conditions the aqueous solution of the container has a pH between 7 and 11.

In another objective according to the invention there is provided in a use of the aqueous solution comprising the sodium salt of the chelating compound of formula I for making an iron-chelate complex. The making of such complexes as such is known in the art, for instance as indicated above in US 5110965. When applying the aqueous HEDTA salt of the invention, it is further clear to the skilled man how to make such complexes. Other metals than iron can also be complexed, such as other Group VIII metals, transition metals, rare earth metals, and the like. If Fe complexes are made the aqueous HEDTA salt solution preferably contains 5-7 wt.% of the iron complex.

It is also an object of the invention to provide a method for making the above-mentioned aqueous HEDTA salt solutions. To this end the invention pertains to a method of preparing an aqueous solution comprising at least 45 wt.% of the sodium salt of the chelating compound of formula I from the trisodium salt of N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid ($\text{Na}_3\text{-HEDTA}$), comprising the step of electrodialysing at ambient temperature an aqueous solution containing less than 42 wt.% of $\text{Na}_3\text{-HEDTA}$, or at a different temperature at maximally the concentration whereby the viscosity is the

ACD 3014 PDEP

4

same, through a bipolar and a cation membrane, thereby converting the $\text{Na}_3\text{-HEDTA}$ solution to the solution of the sodium salt of formula I.

5 The higher the temperature during electrodialysis, the lower the viscosity of the $\text{Na}_3\text{-HEDTA}$ solution. Thus when higher temperatures are selected higher concentrations than 42 wt.% of $\text{Na}_3\text{-HEDTA}$ can be used. However, when the viscosity of the solution becomes higher than the viscosity of a 42 wt.% solution at room temperature, the transport of HEDTA salt through the electrodialysis cell is too much hampered to obtain an efficient process. It is preferred to work at lower temperatures, most preferably at room
10 temperature, for economic reasons and for allowing the use of heat sensitive membrane types.

Electrodialysis processes with bipolar membranes (EDBM) are known in the art. An overview of such processes can be found in Bailly, Desalination, 144,
15 157-162 (2002). When using such process for making the sodium salt of HEDTA, preferably a caustic electrolyte is used, such as sodium or potassium hydroxide, sodium (hydrogen) carbonate, and the like. Suitable bipolar membranes are for instance Neosepta® BP1 from Tokuyama Corporation Ltd. (Japan) or FT-BP™ from FumaTech GmbH (Germany). A cation exchange membrane is used to separate the acid compartment from
20 the base compartment and also to transport the sodium ions from the acid to the base compartment. Cation exchange membranes for this application should be acid and base stable. Suitable cation exchange membranes are for instance Neosepta® CMB (Tokuyama Corp.), FT-FKL™ and FT-FKB™
25 (both FumaTech GmbH) but any other cation exchange membranes can be used as long as these are acid and base stable and stable in the HEDTA solution under the conditions of the electrodialysis process.

The bipolar membrane electrodialysis process can be operated up to 90° C, which is the maximum temperature which most of the cation exchange
30 membranes can stand. Preferably the temperature should be below about 60° C when applying the FumaTech FT-BP™ bipolar membrane or below

ACD 3014 PDEP

5

about 45° C when applying the Tokuyama Corp. Neosepta® BP1E bipolar membrane. From a practical point of view the process is most preferably performed at room temperature.

5 Due to electro-osmosis, water together with the sodium ions migrates to the caustic compartment. The HEDTA concentration therefore increases during the acidification process.

The invention is further illustrated with the following examples.

10 Example 1

A 41 wt.% Na₃-HEDTA solution with pH 11.05 was converted to the compound of formula I by circulation the solution through a bipolar membrane (Neosepta® BP1; ex Tokuyama Corporation Ltd.) electro dialysis stack using a pump. During the process, the pH was measured in the
15 HEDTA compartment. It was found that the pH decreased to 9.6 and that the viscosity decreased to allow the fluid flow to increase from 40 l/h to over 200 l/h at the same other conditions.

Example 2

20 In order to demonstrate that the handling of viscous concentrated HEDTA solutions is influenced by the pH the viscosity of HEDTA solutions was measured over a wide range of concentrations at two different temperatures (20° and 50° C). The advantages of low viscosity are making it easier it to empty drums/containers, flushing lines, maintaining flows during
25 pumping/handling the product, etc.

The Tables below show the viscosity (centiPoise) against HEDTA concentration (as Iron Total Sequestering Value expressed as Na₃-HEDTA salt) for the HEDTA sodium salt in which x=3, x=2.4 and x=2.1 (see Formula I).

ACD 3014 PDEP

6

Table I. Viscosity of HEDTA salts in relation to Fe-TSV at 20° C

Concentration (wt.%)	x=3 viscosity (cP)	x=2.4 viscosity (cP)	x=2.1 viscosity (cP)
10	2	1.8	2
30	7.1	5.2	4.3
40	19	12.7	10
50	∞*	54	32.9

* The viscosity of the HEDTA trisodium salt at 50 wt.% could not be determined due to solidification of the product.

- 5 At low concentration (10 wt.%) there is no difference between Na₃-HEDTA (prior art) and Na_{2.4}-HEDTA and Na_{2.1}-HEDTA (this invention). At higher concentrations the differences become large. At 50 wt.% Na₃-HEDTA cannot be used anymore, whereas both Na_{2.4}-HEDTA and Na_{2.1}-HEDTA can still easily be handled.

10

Table II. Viscosity of HEDTA salts in relation to Fe-TSV at 50° C

Concentration (wt.%)	x=3 viscosity (cP)	x=2.4 viscosity (cP)	x=2.1 viscosity (cP)
10	1.1	1	1.2
30	3.1	2.3	2.3
40	6.7	5.2	4.2
50	21.1	14.2	10.1

At higher temperature (50° C) the viscosity differences between Na₃-HEDTA (prior art) and Na_{2.4}-HEDTA and Na_{2.1}-HEDTA, although smaller than at 20° C, remain.

15

ACD 3014 PDEP

7

Example 4

5 Transport classification of aqueous HEDTA solutions is also linked to corrosive potential. Corrosion tests carried out using a 40 wt.% caustic-free $\text{Na}_3\text{-HEDTA}$ solution on aluminum 7075 T6 showed that the rate of corrosion to aluminum was above the allowed limit (max. average corrosion rate of 6.2 mm/year). This test with a 40 wt.% $\text{Na}_{2.3}\text{H}_{0.7}\text{-HEDTA}$ aqueous solution gave an average corrosion rate for aluminum 7075 T6 of < 1 mm/year. This allows the product to be handled in aluminum containers and production equipment.

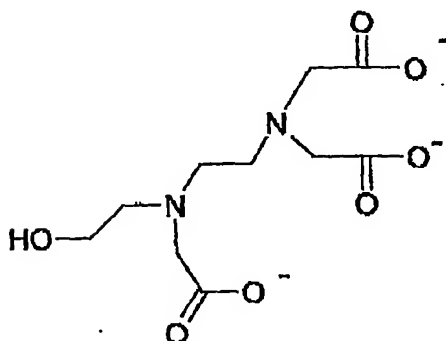
10

ACD 3014 PDEP

8

Claims:

1. A container comprising at least 0.5 kg of an aqueous solution of a sodium salt $x\text{Na}^+ y\text{H}^+$ of the chelating compound of formula I:



- 5 wherein $x = 2.1 - 2.7$, $y = 0.9 - 0.3$, and $x + y = 3$.

2. The container of claim 1 wherein the aqueous solution comprises at least 45 wt.% of the sodium salt of the chelating compound of formula I.

- 10 3. Use of an aqueous solution comprising the sodium salt of the chelating compound of formula I for making an iron-chelate complex.

- 15 4. A method of preparing an aqueous solution comprising at least 45 wt.% of the sodium salt of the chelating compound of formula I from the trisodium salt of N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (Na₃-HEDTA), comprising the step of electrodialysing at ambient temperature an aqueous solution containing less than 42 wt.% of Na₃-HEDTA, or at a different temperature at maximally the concentration whereby the viscosity is the same, through a bipolar and a cation membrane, thereby converting the
- 20 Na₃-HEDTA solution to the solution of the sodium salt of formula I.

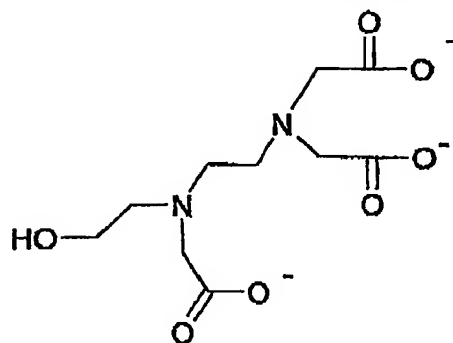
5. The method according to claim 4 wherein a caustic electrolyte is used.

ACD 3014 PDEP

9

Abstract

The invention relate to a container comprising at least 0.5 kg of an aqueous solution of a sodium salt $x\text{Na}^+ y\text{H}^+$ of the chelating compound of formula I:



5

wherein $x = 2.1 - 2.7$, $y = 0.9 - 0.3$, and $x + y = 3$. The invention further pertain to a method of preparing an aqueous solution comprising at least 45 wt.% of the sodium salt of the chelating compound of formula I from the trisodium salt of N-hydroxyethylenediamine-N,N',N'-triacetic acid (Na₃-HEDTA), comprising the steps of electrodialysing an aqueous solution containing less than 42 wt.% of the trisodium salt through a bipolar membrane, thereby converting the trisodium salt solution to the solution of the sodium salt of formula I.

10

PCT/EP2004/007841



**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☒ FADED TEXT OR DRAWING

☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☒ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.